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CONTROLLED SYNTHESIS OF ORGANIC-INORGANIC POLYMERS THAT POSSESS--ETC(U)
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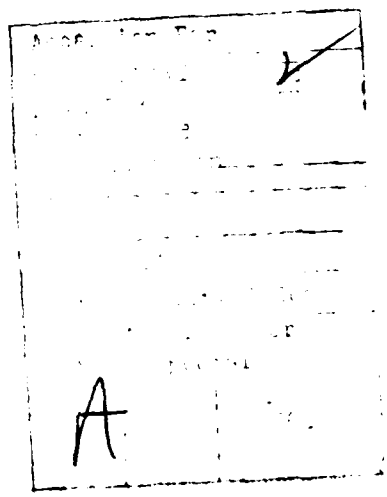

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CONTROLLED SYNTHESIS OF ORGANIC-INORGANIC POLYMERS THAT POSSESS A BACKBONE OF PHOSPHORUS AND NITROGEN ATOMS

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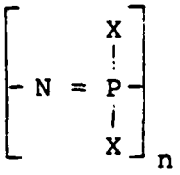
Abstract - A new class of macromolecules has been synthesized based on a skeletal structure of alternating phosphorus and nitrogen atoms (I). These are the first high polymers with an inorganic backbone to be developed on a broad scale since the discovery of the poly(organosiloxanes) in the 1940's.



(X = Halogen or Organic, n≈15,000)

I

The preferred synthesis route makes use of highly reactive polymeric intermediates (I, X = Cl or F) used as substrates for halogen replacement by organic nucleophiles. Structural diversity is achieved either by changes in the nucleophile or by chemical modification of the side groups after they are attached to the backbone. Using these principles, a wide range of different polymers has been prepared ranging from elastomers to carrier molecules for steroids, transition metals, metalloporphyrins, or carboranes. Biodegradable and biocompatible macromolecules have also been synthesized. The critical role of small molecule model reactions is stressed, and examples are given of recently discovered organometallophosphazenes that are expected to have a profound influence on future polyphosphazene syntheses.

Future developments in both the science and technology of macromolecules may depend on the availability of polymers that are drastically different from those that are familiar at the present time. Specifically, a growing interest exists in the design and synthesis of polymers with extremely flexible molecular structures on the one hand, or rigid, extended chain conformations on the other. A need exists for other materials that conduct electricity or can function as carrier molecules for biologically active or organometallic agents. Moreover, a long-range interest exists in the use of the controlled

sequencing of side groups along a polymer chain for information storage or template syntheses.

In our laboratory we are testing the idea that such alterations in bulk properties and individual macromolecular behavior can be accomplished by drastic changes in the macromolecular backbone; in other words, by the incorporation of inorganic elements into the chain structure.

Inherent in this approach is the need to separate the construction of the polymer chain from the attachment of specific side groups to the chain. The most characteristic feature of conventional macromolecular synthesis is that changes in polymer side group structure are accomplished by modifications to the polymerization process, i.e. by changes in the monomer used, by copolymerization, or by variations in the initiator or the polymerization conditions.

The alternative approach to macromolecular diversity is based not on changes in the polymerization process, but on the replacement of one side group structure by another after the polymer chain has been constructed. We will call this the substitutive approach to polymer synthesis. This approach is not new, but it is relatively uncommon and is employed mainly in long-established and well-known processes such as conversion of poly(vinyl acetate) to poly(vinyl alcohol), the chemical modification of cellulose, and the chloromethylation of polystyrene. As will be discussed, the realities of inorganic chemistry require that this approach must usually be employed for the preparation of new inorganic chain polymers with organic side groups.

Because of the need for a substitutive approach to the synthesis of inorganic-type macromolecules, two serious problems must be taken into account. First, substitution reactions carried out with a macromolecular substrate may be retarded by chain coiling, adjacent charge effects, or solvent-polymer interactions. Hence, highly reactive macromolecular substrates may be needed before such an approach is feasible. Second, the substitution reactions must be exceedingly "clean" in the sense that skeletal cleavage or molecular coupling side reactions can have a catastrophic effect on the macromolecular substrate. Hence, our approach to this problem has depended on the extensive use of small-molecule analogues as models for the design of macromolecular substitution reactions (Ref. 1).

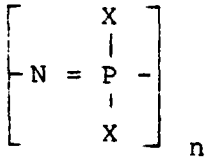
MOLECULAR DESIGN (GENERAL)

We begin with the requirement that the macromolecular system should be based on an inherently flexible skeletal structure, since reduced flexibility or high rigidity can be ensured later, if necessary, by the choice of bulky or hydrogen bonded side groups. A second requirement for certain properties is the existence of an unsaturated bonding mode in the backbone, preferably comprising a broadly delocalized electronic arrangement. Third, and most critical, is the need for a reactive polymeric substrate that will allow the selective attachment of a wide range of side groups to the backbone. And fourth, reactions must be available for the facile

attachment of side groups that will confer hydrophobicity, hydrophilicity, water- or organic-solubility on the system, or will allow the linkage of "active" side groups such as transition metals, biologically-active units, metalloporphyrins, chromophores, etc. These requirements are met by a macromolecular system based on a chain of alternating phosphorus and nitrogen atoms. They are called polyphosphazenes.

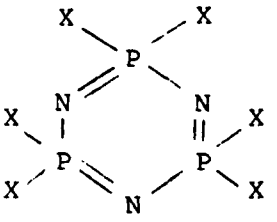
CHARACTERISTICS OF POLYPHOSPHAZENES (GENERAL)

The basic structure of polyphosphazenes is illustrated by structure I.

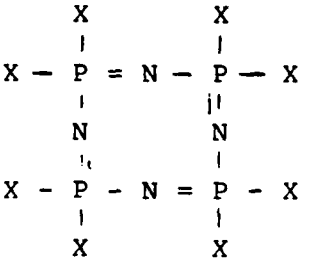


(n≈15,000)

I



II



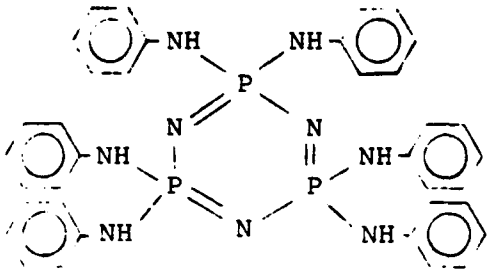
III

Although the chemistry of these high polymeric species is of fairly recent origin, small-molecule analogues, such as II and III (X = Cl) have been known since the early 1800's (Ref. 2). They are prepared by the reaction between phosphorus pentachloride and ammonium chloride in an organic solvent (Ref. 3). As long ago as 1897 Stokes (Ref. 4) recorded that the heating of II or III brought about its conversion to an insoluble rubbery elastomer. Physical characterization of this polymer was attempted by later investigators (Refs. 5 & 6), but its insolubility prevented any definitive chemical exploration.

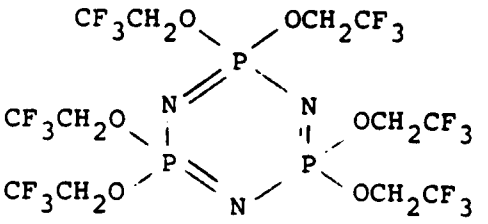
However, it was clear from the early work that the polyphosphazene system possessed some of the key requirements listed above for the development of a new macromolecular system - a highly flexible backbone system (as indicated by the rubbery elasticity of the insoluble $(NPCl_2)_n$, I), a formally unsaturated skeleton, highly reactive side group bonds (as evidenced by the hydrolytic instability of I), and the possible adaptability of I to the nucleophilic replacement of chlorine by hydrolytically stable organic residues.

MODEL COMPOUND STUDIES

Initially, it was found that the cyclic oligomers (I and II) could function as substrates for the nucleophilic replacement of chlorine by amino (IV), alkoxy (V), or aryloxy groups without detectable chain cleavage or intermolecular linkage



IV



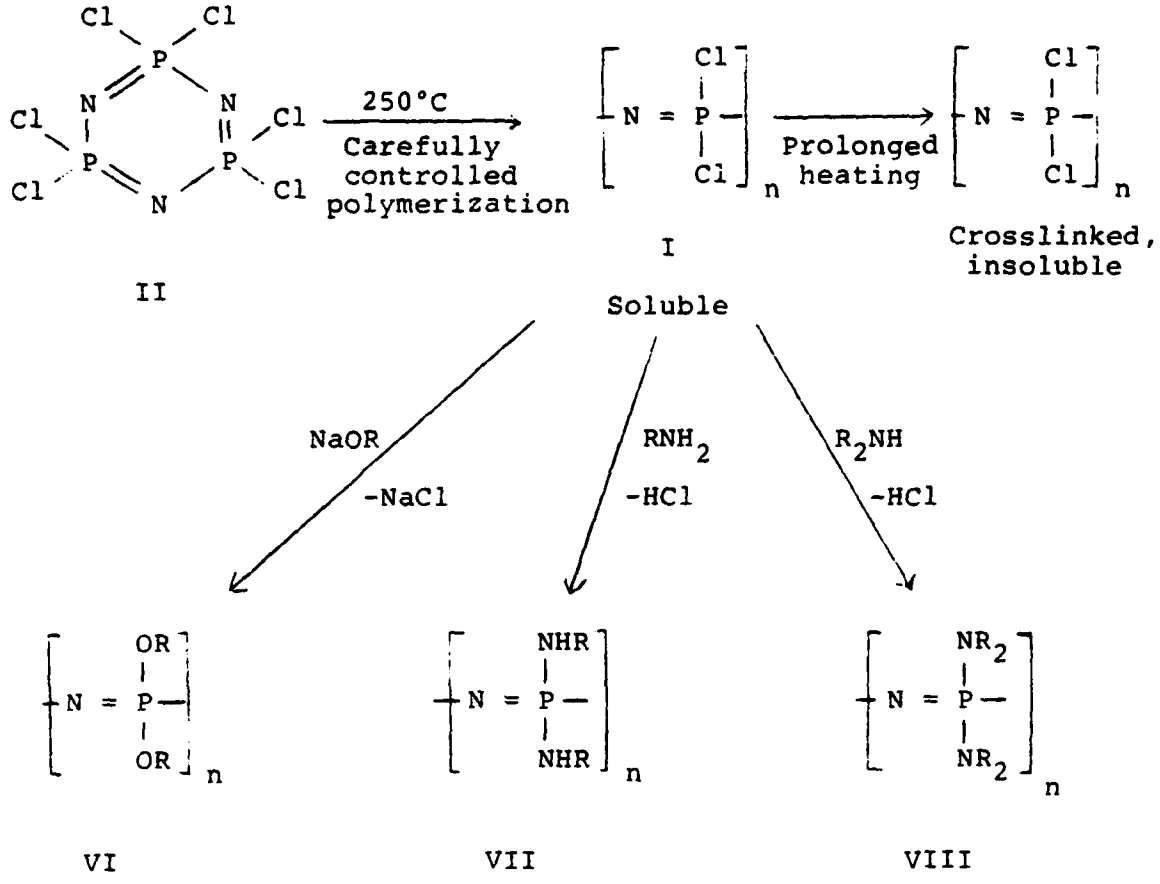
V

(Refs. 7-10). Large numbers of such cyclic derivatives have now been prepared (Ref. 11). These reactions have played a vital part in the design of the more challenging macromolecular syntheses (Ref. 1). Nevertheless, an extension of these reactions to the high polymer could not be made until a method was found for the preparation of a soluble form of I.

BACKGROUND TO THE SUBSTITUTIVE APPROACH TO POLYPHOSPHAZENES

Insolubility in a linear type polymer can generally be attributed to high crystallinity, excessive chain branching, or crosslinking. Because poly(dichlorophosphazene) is amorphous at room temperature in the unstretched state, this factor can be excluded. Thus, it appeared possible that the original forms of poly(dichlorophosphazene) were excessively branched, crosslinked, or both. It was reasoned that if the chain branching and/or crosslinking reactions were kinetically distinct from chain propagation, it might be possible to terminate the polymerization reaction before insolubilization took place. This idea proved to be correct (Refs. 12-14). In a typical polymerization reaction, the insoluble polymer is formed only after ≈70% of the cyclic trimer has been converted to polymer. The high polymer isolated before this stage is completely soluble in solvents such as benzene or tetrahydrofuran. This observation provided the key to all the subsequent synthetic work on polyphosphazenes.

Soluble poly(dichlorophosphazene) is highly reactive to nucleophilic substitution reactions. The initial experiments showed that all the chlorine atoms in I can be replaced by OCH_3, OC_2H_5, OCH_2CF_3, OC_6H_5, NHC_6H_5, NHC_2H_5, $N(CH_3)_2$, or NC_5H_{10} (piperidino) groups, without crosslinking and, in most cases, without chain cleavage (Refs. 12-14). These reactions are summarized in Scheme 1. Needless to say, this cannot be accomplished with the crosslinked form of I.



II I VI VII VIII

R = organic. n ≈ 15,000

Scheme 1

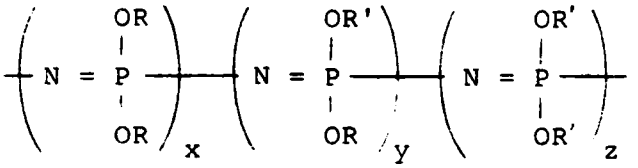
The prototype homopolymers, VI, VII, and VIII are stable to water, soluble in various solvents, and have properties that depend on the side group structure. For example, species with OR = OCH_3 or OC_2H_5 are elastomers (Tg, -70°C and -84°C, respectively); the derivative with OR = OCH_2CF_3 is a hydrophobic, microcrystalline, film- and fiber-forming polymer (Tg, -66°C). When OR = OC_6H_5 the polymer is a microcrystalline thermoplastic (Tg, -8°C). Anilino side groups generate glass-like properties. The CH_3NH group provides solubility in water (Ref. 15). Most of these polymers resist burning. A substantial number of homopolymers have now been reported (Refs. 16-20), and a number of these have been subjected to structural analysis. Certain aryloxy derivatives show evidence of liquid crystalline behavior (Refs. 21 & 22).

CONTROLLED SYNTHESIS BY SUBSTITUTION

Although the homopolymers derived from Scheme 1 are themselves of continuing interest from both the fundamental and applied viewpoints, special attention has been paid to the preparation of mixed-substituent polyphosphazenes. One of the advantages of the polyphosphazene system is the ease with which two or more different substituents can be introduced, often in a controlled manner. The following examples illustrate this feature.

Mixed substituent elastomers

Many phosphazene homopolymers are highly microcrystalline and therefore behave as flexible thermoplastics at room temperature rather than elastomers (see note a). Crystallization depends, of course, on stereochemical order. Hence, a disruption of molecular symmetry leads to a reduction in or a loss of microcrystallinity. This principle was first demonstrated by the competitive cosubstitution of $(NPCl_2)_n$ by two different nucleophiles, for example, by CF_3CH_2ONa and $CF_3CF_2CH_2ONa$ (Ref. 25). Although the two homopolymers are non-elastomeric, the mixed substituent polymer is a solvent-resistant, low temperature elastomer. Different aryloxy groups attached to the same chain can generate a similar effect (Refs. 26-30), and these elastomers have stimulated a growing technological interest. An alternative method exists to achieve the same end - the metathetical replacement of one organic substituent by another (Ref. 31). The structure of the mixed substituent elastomers is quite complex, with all three of the possible repeating sequences shown in IX probably being present.



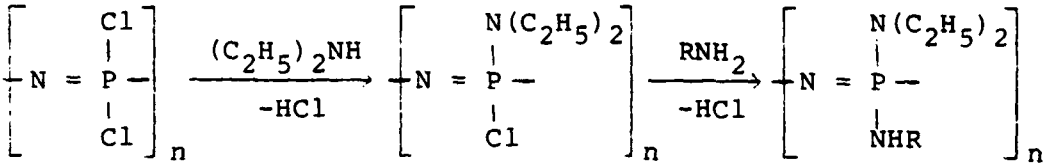
IX

The elastomeric behavior of these derivatives is not fully understood but is of continuing interest.

Note a. Exceptions are $(NPF_2)_n$ and $(NPCl_2)_n$ which crystallize only when stretched or cooled (Refs. 23 & 24), and $[NP(OCH_3)_2]_n$, or $[NP(OC_2H_5)_2]_n$ which appear to resist crystallization (Refs. 13 & 19), presumably because of the high conformational mobility of the side groups.

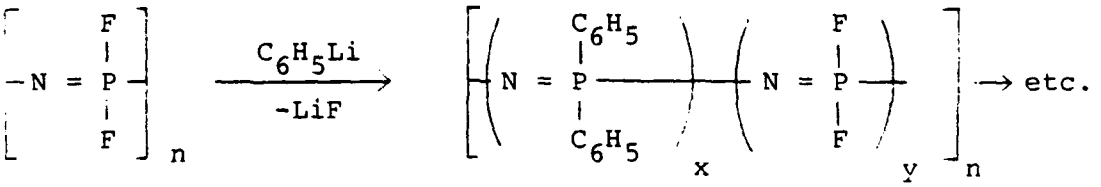
Non-geminal and geminal synthesis

Although competitive cosubstitution or metathetical exchange leads mainly to a randomization of sterochemical structure, sequential substitution can generate structural order. For example, diethylamine reacts with $(NPCl_2)_n$ to replace only 50% of the chlorine atoms, apparently to yield the non-geminal structure, X (Ref. 15).



I X XI

The remaining chlorine atoms can then be replaced by a second organic group to yield species, such as XI. However, no evidence exists yet that isotactic or syndiotactic-type order is present in these molecules. Some evidence has been obtained that the reaction of $(NPCl_2)_n$ with aryloxide proceeds by a non-geminal route. For example, the treatment of $(NPCl_2)_n$ with one equivalent per repeating unit of phenoxide ion, followed by an excess of p-bromophenoxide ion, yields a mainly non-geminal substituent array (Refs. 32 &33). By contrast, evidence has been obtained that the reaction of phenyllithium with $(NPF_2)_n$ (XII) proceeds initially by a geminal replacement pattern (XIII) (Ref. 34).



XII XIII

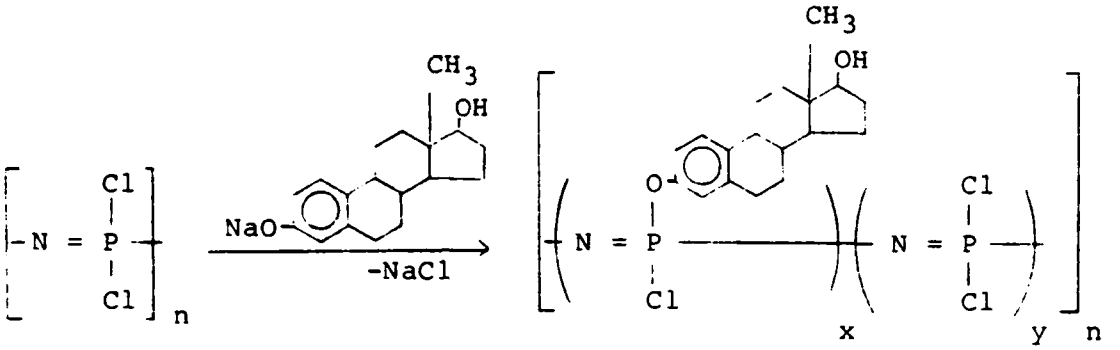
With diethylaminolysis and aryloxide attack, the non-geminal pattern is probably caused by steric effects. However, electronic effects must be invoked to explain the geminal pathway with phenyllithium.

It should be noted that poly(difluorophosphazene)(XII) is a preferred substrate for organometallic substitution reactions because it is less prone to skeletal cleavage reactions with strong nucleophiles than is poly(dichlorophosphazene) (Ref. 34).

Attachment of "active" substituent groups

The use of macromolecules as "carrier molecules" for catalytically active or biologically active small molecule species is well known. Polyphosphazenes possess definite advantages as carrier molecules because of the ease with which active substituent groups can be attached to the skeleton and (as will be illustrated later) because of the possibility that biodegradability can be ensured by the choice of a suitable cosubstituent unit. Five examples will be given here to illustrate the scope of this approach.

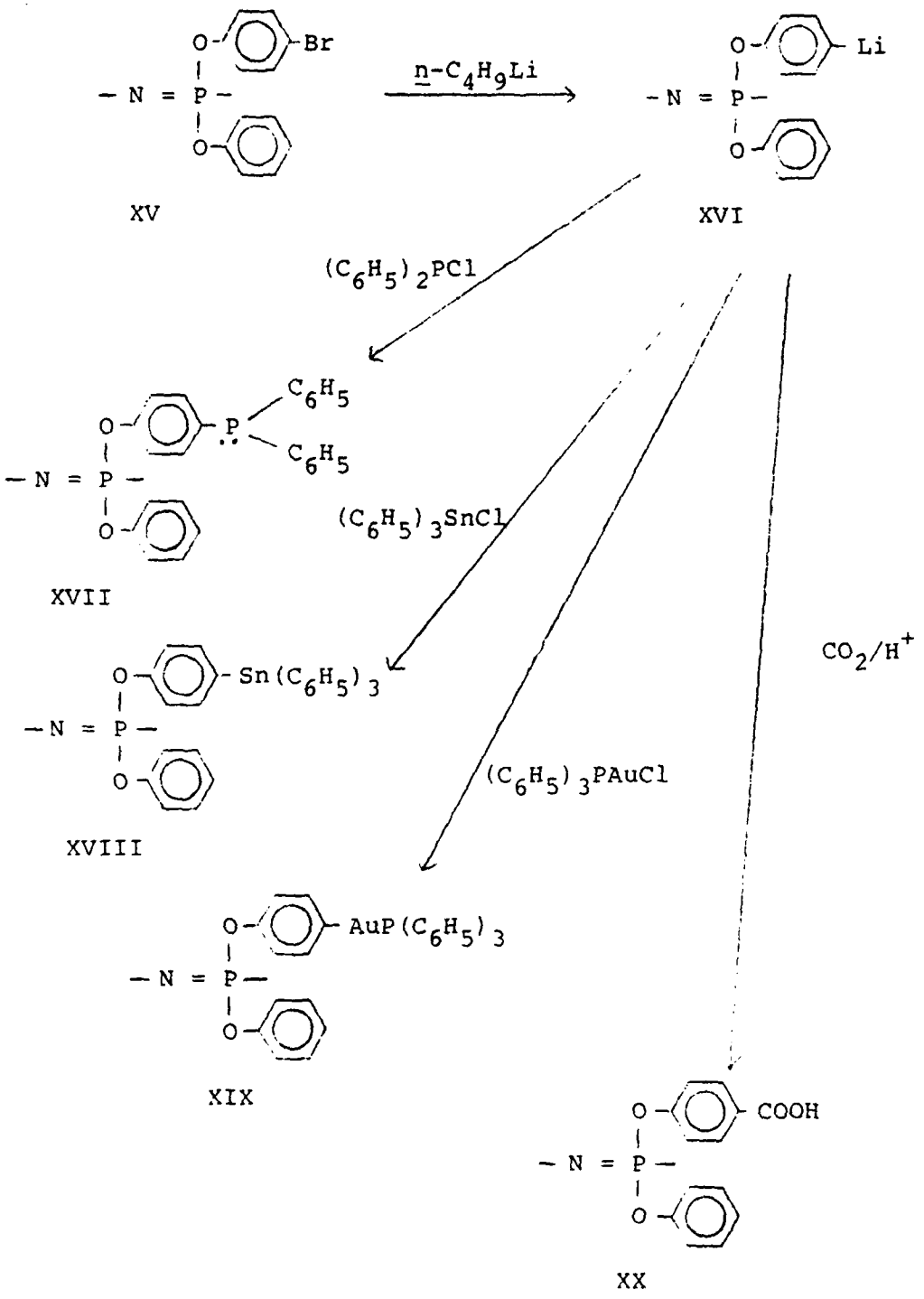
First, a successful attempt has been made recently to attach steroid molecules to a polyphosphazene chain. This can be accomplished via the sodium salts of steroids that possess a hydroxyl group at the 3-position (Ref. 35), as shown in the formation of XIV.



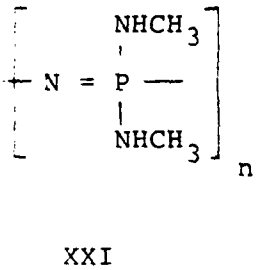
XIV

The steroidoxide ion behaves as a bulky aryloxide analogue, with the expected steric limits to complete chlorine replacement. The remaining chlorine atoms can be replaced by water solubilizing units ($NHCH_3$) or biologically compatible and degradable side groups, such as amino acid ester residues (see later). Interestingly, the steroid coupling reaction to $(NPCl_2)_n$ does not occur if the A-ring is saturated. In such cases the $(NPCl_2)_n$ acts as a dehydrating agent for the steroid.

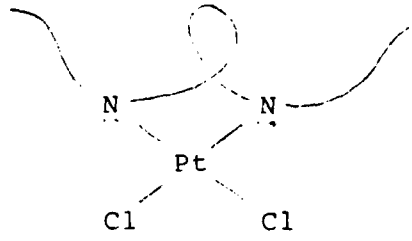
Second, active groups can be attached to the polymer via reactions that are carried out on the perimeter of side groups already present. As mentioned earlier, polyphosphazenes can be prepared by the controlled attachment of phenoxy and p-bromophenoxy groups to the skeleton (XV). A metal-halogen exchange reaction can then be carried out to yield XVI, which functions as a polymeric organometallic intermediate for the preparation of species XVII-XX (Refs. 32 &33). Species XVII is a carrier molecule for transition metal catalyst systems.


Br
n-C4H9Li
Li
XV
XVI
(C6H5)2PCl
C6H5
C6H5
XVII
(C6H5)3SnCl
CO2/H+
Sn(C6H5)3
XVIII
(C6H5)3PAuCl
AuP(C6H5)3
XIX
COOH
XX

Third, the coordination ability of polyphosphazenes can be exploited in another way. The backbone nitrogen atoms are sufficiently basic that they can function as coordinative donor sites for transition metals. Perhaps the best example of this, to date, is the ability of carrier polymer XXI to bind



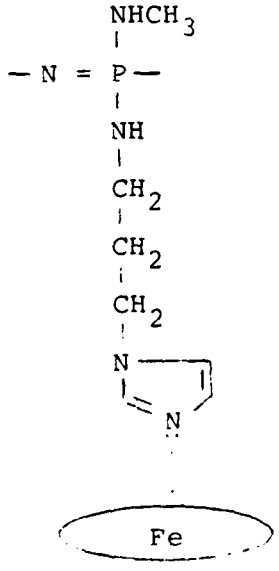
XXI



XXII

square planar platinum species (XXII) (Ref. 36). In this way the polymer may alleviate some of the physiological side reactions encountered when platinum compounds are employed in antitumor therapy.

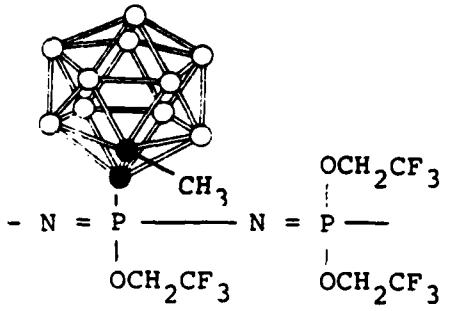
A fourth approach to the attachment of active side group structures is of special interest for the binding of metalloporphyrins. Units of type XXIII can be incorporated into a polyphosphazene structure by the sequential reaction of $(NPCl_2)_n$ with $NH_2\text{-}(CH_2)_3\text{-}C_3N_2H_3$ and methylamine (Ref. 37).



XXIII

Such polymers are water-soluble and bind strongly to metalloporphyrins, such as heme or hemin. In a sense, they function as model "polypeptide analogues", and allow the protective role of the polymer in solution to be explored. Some evidence also exists that the polyphosphazene has a capacity to reduce Fe(III) to Fe(II). Carrier polymer XXI does not bind strongly to heme or hemin, even though it possesses skeletal donor sites.

And fifth, although not an "active" unit in a conventional sense, stabilizing units of the carborane type can be attached to the skeleton by organometallic reactions. For example, the lithio-derivative of methylcarborane reacts with $(NPCl_2)_n$ to yield polymers of structure XXIV (Ref. 38). These are considered to be exploratory precursors for the attachment of catalytically active metallo-carborane units.



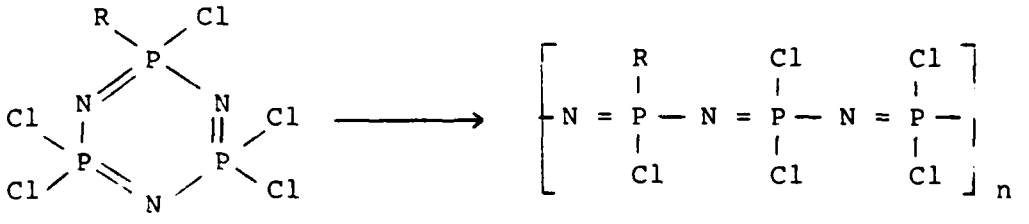
XIV

CONTROLLED SYNTHESIS BY POLYMERIZATION

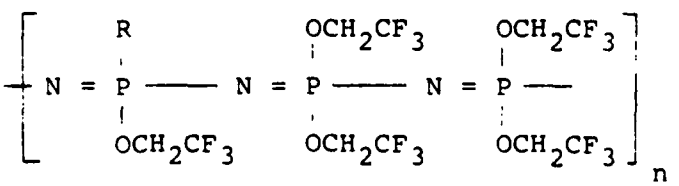
The substitutive approach to polyphosphazene preparation remains the most important method for controlled synthesis. However, recently a few new types of polyphosphazenes have been prepared by changes in the polymerization process, followed by substitutive modification. This provides a new dimension to the preparation of phosphazene polymers.

An early problem with the preparation of polyphosphazenes was the observation that, although halogenocyclophosphazenes, such as $(NPF_2)_3$, $(NPCl_2)_3$, or $(NPBr_2)_3$ polymerize thermally, cyclic phosphazenes that bear organic side groups do not. Trimers, such as $[NP(CH_3)_2]_3$, $[NP(OCH_2CF_3)_2]_3$, $[NP(OC_6H_5)_2]_3$, or $[NP(C_6H_5)_2]_3$ may undergo ring-ring equilibration, but they do not yield high polymers (Refs. 39-41). Thermodynamic and mechanistic arguments have been put forward to explain this (Ref. 42). However, if the trimeric ring bears both halogeno and organic substituents, polymerization may be possible.

For example, monoalkylpentachlorocyclotriphosphazenes (XXV, where R = CH_3, C_2H_5 etc.)polymerize thermally to yield macro-

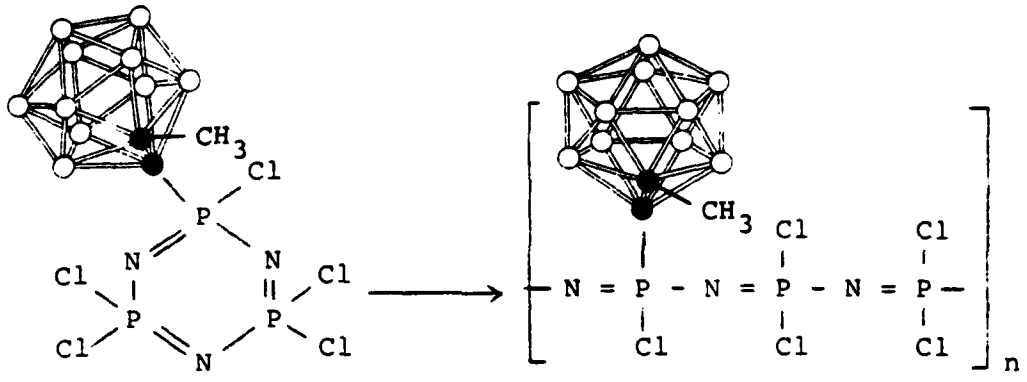


XXV XXVI



XXVII

molecules XXVI, which can be modified by substitutive methods (Ref. 43). The disruption of molecular symmetry in species XXVII allows them to behave as elastomers, for similar reasons to those discussed earlier. A related polymerization has recently been carried out for carboranyl-substituted phosphazene trimers, XXVIII (Ref. 38).



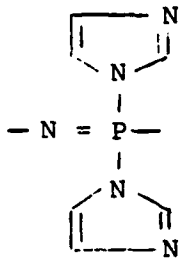
XXVIII

Trimers such as $N_3P_3CH_3Cl_5$, $N_3P_3(C_6H_5)_2Cl_4$, or $N_3P_3(OCH_2CF_3)_6$ undergo thermal copolymerization with $(NPCl_2)_3$ (Refs. 40, 41, 43). These observations suggest that the presence of P-Cl bonds in the system is a prerequisite for chain propagation, perhaps because of the capacity of P-Cl bonds to ionize thermally (Ref. 44) or the facility with which traces of water can induce hydrolysis to P-OH units (Refs. 41 &45).

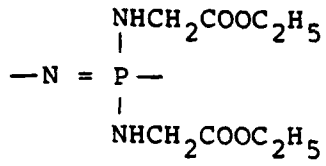
ADVANCED DEVELOPMENTS

As illustrated, the pattern of synthetic advances in this field depends heavily on new discoveries at the small molecule level. Hence, pointers for future developments at the macromolecular level may be found in recent cyclophosphazene research.

First, recent work has shown that two classes of aminocyclophosphazenes hydrolyze readily to phosphate, ammonia, and the free side group at biological pH conditions in a manner that suggests promise for the preparation of biodegradable polymers. The hydrolytically sensitizing side groups are the imidazole group and various amino acid ester units, both linked through nitrogen to phosphorus (XXIX and XXX) (Refs. 46 & 47). This has wide-ranging implications for the design of carrier polymers for the slow release of drug molecules.

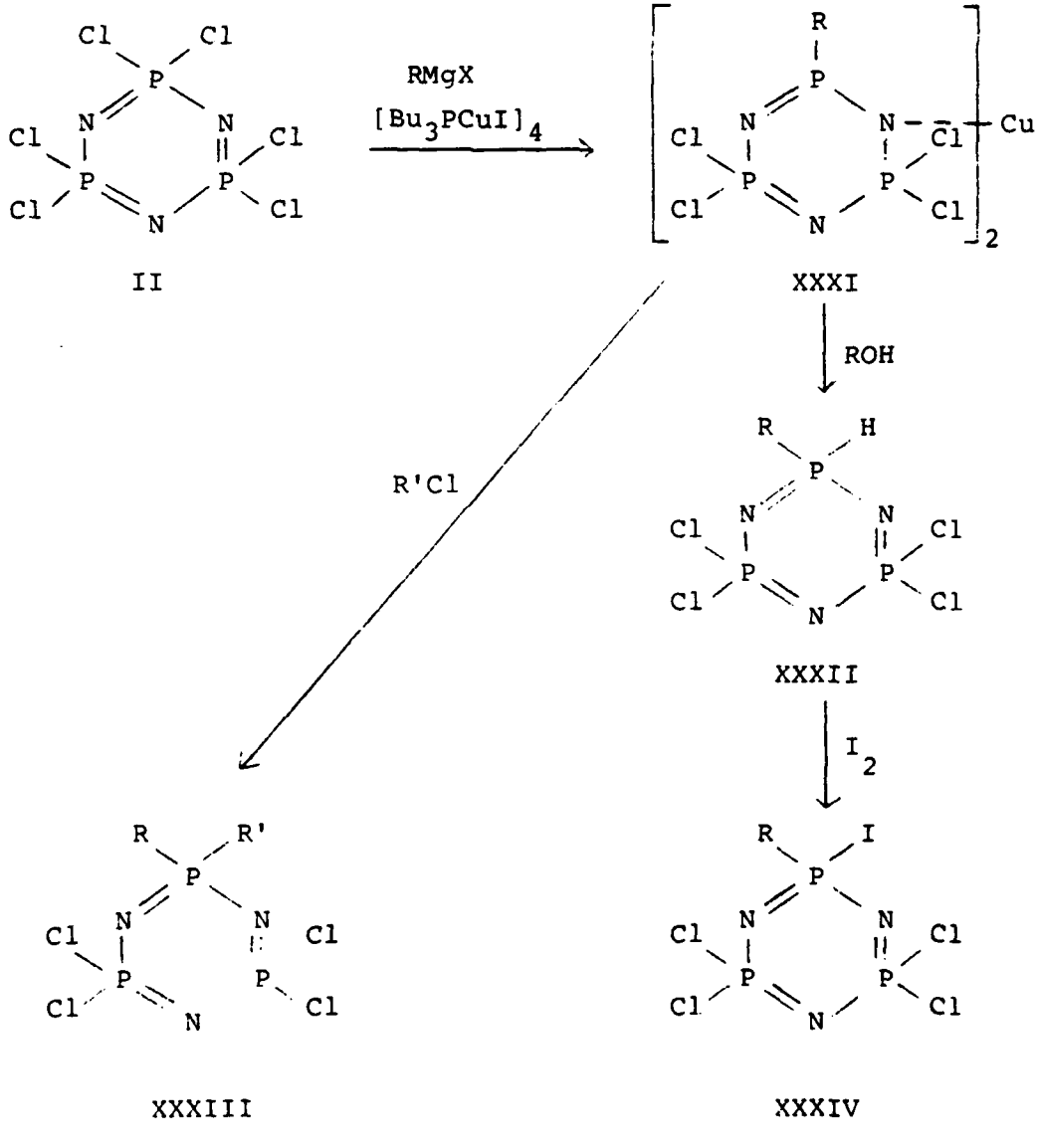


XXIX



XXX

Second, it is now possible at the cyclic oligomer level to introduce hydrogen as a substituent group. This has been accomplished via organometallic reactions of the type shown for the conversion of II to XXXII (Ref. 48).



II

XXXI

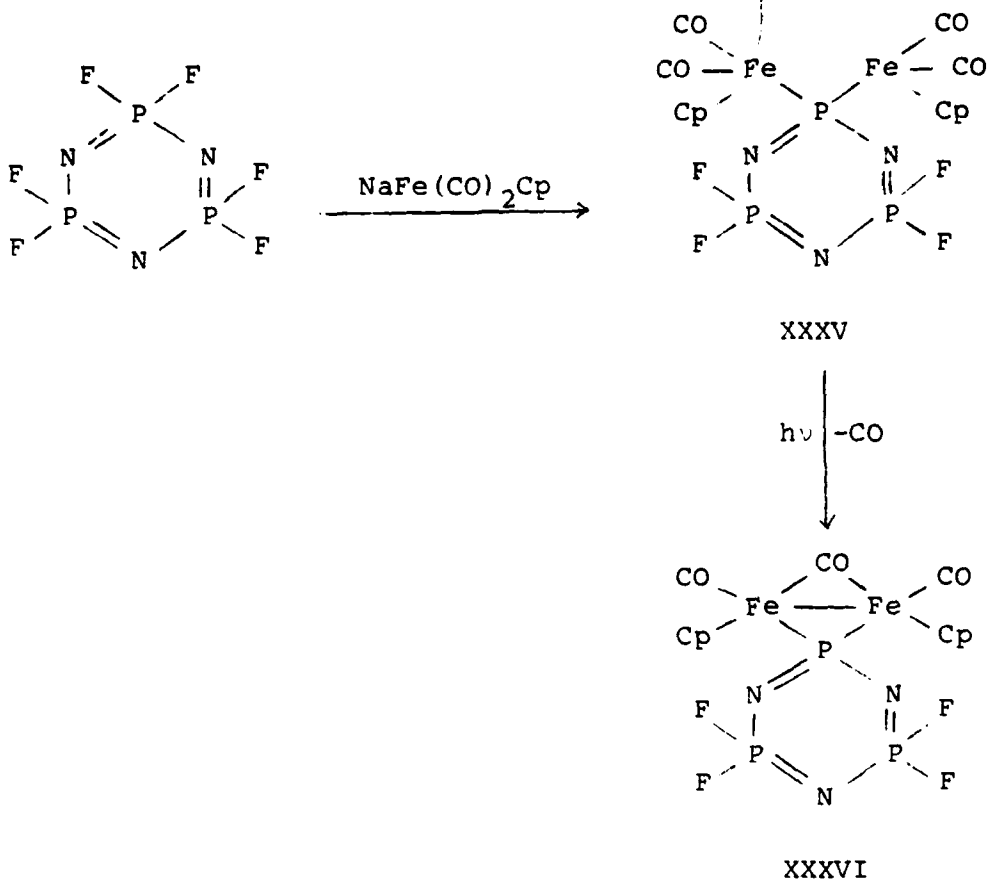
XXXII

XXXIII

XXXIV

Because of the high reactivity of XXXI and XXII, these species can be used an intermediates for the introduction of, for example, unsaturated alkyl groups, R' (XXXIII) (Ref. 49) or iodine as a side group (XXXIV). Unsaturated side groups provide a π-ligand site for the binding of transition metals (Ref. 50).

Third, it has recently been shown that phosphazenes with direct phosphorus-metal side group units can be prepared by the interaction of $(NPCl_2)_3$ with organometallic reagents, as in the formation of XXXV and XXXVI (Ref. 51).



XXXV

XXXVI

The implications of structure XXXVI in a polymeric system are quite far-reaching.

SUMMARY OF PRESENT IDEAS AND FUTURE PROSPECTS

The developments seen so far in polyphosphazene chemistry reinforce the view that drastic changes in the backbone structure of macromolecules bring forth a whole range of new and often unexpected phenomena. It seems clear that the construction of new polymer systems based on other combinations of the inorganic elements is a worthwhile challenge for the future. Meanwhile, the synthetic and structural ramifications of the polyphosphazene system have hardly been touched by the present work, and it seems clear that this field may develop into a major area of polymer chemistry. Well over 100 different poly(organo)-

phosphazenes) have been synthesized and characterized, and this represents only a small fraction of those that are accessible even with known techniques. Certain lessons can be learned from the development of the poly(organophosphazene) field. First, the long-standing preoccupation of polymer chemists with petroleum-based monomers and polymers is the result of traditional rather than practical restrictions. Inorganic chains can display all the structural and physicochemical attributes of carbon-based chains and can, at the same time, offer intriguing new phenomena. This was recognized many years ago by workers in polysiloxane chemistry, but the generality of this idea is only slowly gaining acceptance.

Second, the discovery and development of new inorganic-based macromolecular systems need not be inhibited by the failure of most potential monomers to polymerize. Provided one or two monomers or cyclic oligomers with the required skeletal structure can be converted to a linear high polymer, other species can be generated by substitutive (or additive) methods. This is a key concept for the future development of this field.

And finally, because inorganic small-molecule ring systems are much more readily available at present than are the analogous high polymers, it is essential that the reactivities of these models should be explored in detail. This seemingly indirect approach is an essential prerequisite for the synthesis of high polymeric analogues.

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